

FORM PTO-1390 (Modified)  
(REV 10-95)

U.S. DEPARTMENT OF COMMERCE PATENT AND TRADEMARK OFFICE

ATTORNEY'S DOCKET NUMBER

## TRANSMITTAL LETTER TO THE UNITED STATES

MERCK 2038

DESIGNATED/ELECTED OFFICE (DO/EO/US)

U.S. APPLICATION NO. (IF KNOWN, SEE 37 CFR

CONCERNING A FILING UNDER 35 U.S.C. 371

09/446326

INTERNATIONAL APPLICATION NO.

PCT/EP98/03250

INTERNATIONAL FILING DATE

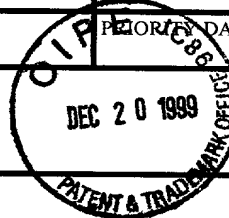
30 MAY 1998

PRIORITY DATE CLAIMED

19 JUNE 1997

TITLE OF INVENTION

LASER-MARKABLE PLASTICS



APPLICANT(S) FOR DO/EO/US

Reiner DELP. et al.

Applicant herewith submits to the United States Designated/Elected Office (DO/EO/US) the following items and other information:

1. ☒ This is a **FIRST** submission of items concerning a filing under 35 U.S.C. 371.
2. ☐ This is a **SECOND** or **SUBSEQUENT** submission of items concerning a filing under 35 U.S.C. 371.
3. ☐ This is an express request to begin national examination procedures (35 U.S.C. 371(f)) at any time rather than delay examination until the expiration of the applicable time limit set in 35 U.S.C. 371(b) and PCT Articles 22 and 39(1).
4. ☒ A proper Demand for International Preliminary Examination was made by the 19th month from the earliest claimed priority date.
5. ☒ A copy of the International Application as filed (35 U.S.C. 371 (c) (2))
  - a. ☐ is transmitted herewith (required only if not transmitted by the International Bureau).
  - b. ☒ has been transmitted by the International Bureau.
  - c. ☐ is not required, as the application was filed in the United States Receiving Office (RO/US).
6. ☒ A translation of the International Application into English (35 U.S.C. 371(c)(2)).
7. ☐ A copy of the International Search Report (PCT/ISA/210).
8. ☒ Amendments to the claims of the International Application under PCT Article 19 (35 U.S.C. 371 (c)(3))
  - a. ☐ are transmitted herewith (required only if not transmitted by the International Bureau).
  - b. ☐ have been transmitted by the International Bureau.
  - c. ☐ have not been made; however, the time limit for making such amendments has NOT expired.
  - d. ☒ have not been made and will not be made.
9. ☐ A translation of the amendments to the claims under PCT Article 19 (35 U.S.C. 371(c)(3)).
10. ☒ An oath or declaration of the inventor(s) (35 U.S.C. 371 (c)(4)).
11. ☐ A copy of the International Preliminary Examination Report (PCT/IPEA/409).
12. ☐ A translation of the annexes to the International Preliminary Examination Report under PCT Article 36 (35 U.S.C. 371 (c)(5)).

## Items 13 to 18 below concern document(s) or information included:

13. ☐ An Information Disclosure Statement under 37 CFR 1.97 and 1.98.
14. ☐ An assignment document for recording. A separate cover sheet in compliance with 37 CFR 3.28 and 3.31 is included.
15. ☒ A **FIRST** preliminary amendment.  
A **SECOND** or **SUBSEQUENT** preliminary amendment.
16. ☐ A substitute specification.
17. ☐ A change of power of attorney and/or address letter.
18. ☐ Certificate of Mailing by Express Mail
19. ☒ Other items or information:

Letter

U.S. APPLICATION NO. (IF KNOWN, SEE 37 CFR 1.53) <b>09/446326</b>		INTERNATIONAL APPLICATION NO. <b>PCT/EP98/03250</b>		ATTORNEY'S DOCKET NUMBER <b>MERCK 2038</b>	
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20. The following fees are submitted: <b>BASIC NATIONAL FEE ( 37 CFR 1.492 (a) (1) - (5)) :</b> <input checked="" type="checkbox"/> Search Report has been prepared by the EPO or JPO ..... <b>\$840.00</b> <input type="checkbox"/> International preliminary examination fee paid to USPTO (37 CFR 1.482) ..... <b>\$670.00</b> <input type="checkbox"/> No international preliminary examination fee paid to USPTO (37 CFR 1.482) but international search fee paid to USPTO (37 CFR 1.445(a)(2)) ..... <b>\$760.00</b> <input type="checkbox"/> Neither international preliminary examination fee (37 CFR 1.482) nor international search fee (37 CFR 1.445(a)(2)) paid to USPTO ..... <b>\$970.00</b> <input type="checkbox"/> International preliminary examination fee paid to USPTO (37 CFR 1.482) and all claims satisfied provisions of PCT Article 33(2)-(4) ..... <b>\$96.00</b>  <b>ENTER APPROPRIATE BASIC FEE AMOUNT =</b>				<b>CALCULATIONS PTO USE ONLY</b>	
				<b>\$840.00</b>	
Surcharge of <b>\$130.00</b> for furnishing the oath or declaration later than months from the earliest claimed priority date (37 CFR 1.492 (e)). <input type="checkbox"/> 20 <input type="checkbox"/> 30				<b>\$0.00</b>	
CLAIMS	NUMBER FILED	NUMBER EXTRA	RATE		
Total claims	12 - 20 =	0	x \$18.00	<b>\$0.00</b>	
Independent claims	1 - 3 =	0	x \$78.00	<b>\$0.00</b>	
Multiple Dependent Claims (check if applicable). <input type="checkbox"/>				<b>\$0.00</b>	
<b>TOTAL OF ABOVE CALCULATIONS =</b>				<b>\$840.00</b>	
Reduction of 1/2 for filing by small entity, if applicable. Verified Small Entity Statement must also be filed (Note 37 CFR 1.9, 1.27, 1.28) (check if applicable). <input type="checkbox"/>				<b>\$0.00</b>	
<b>SUBTOTAL =</b>				<b>\$840.00</b>	
Processing fee of <b>\$130.00</b> for furnishing the English translation later than months from the earliest claimed priority date (37 CFR 1.492 (f)). <input type="checkbox"/> 20 <input type="checkbox"/> 30				<b>\$0.00</b>	
<b>TOTAL NATIONAL FEE =</b>				<b>\$840.00</b>	
Fee for recording the enclosed assignment (37 CFR 1.21(h)). The assignment must be accompanied by an appropriate cover sheet (37 CFR 3.28, 3.31) (check if applicable). <input type="checkbox"/>				<b>\$0.00</b>	
<b>TOTAL FEES ENCLOSED =</b>				<b>\$840.00</b>	
				Amount to be: refunded	\$
				charged	\$

<input checked="" type="checkbox"/>	A check in the amount of <b>\$840.00</b>	to cover the above fees is enclosed.
<input type="checkbox"/>	Please charge my Deposit Account No. _____ in the amount of _____ A duplicate copy of this sheet is enclosed.	to cover the above fees.
<input checked="" type="checkbox"/>	The Commissioner is hereby authorized to charge any fees which may be required, or credit any overpayment to Deposit Account No. <b>13-3402</b> A duplicate copy of this sheet is enclosed.	

**NOTE: Where an appropriate time limit under 37 CFR 1.494 or 1.495 has not been met, a petition to revive (37 CFR 1.137(a) or (b)) must be filed and granted to restore the application to pending status.**

SEND ALL CORRESPONDENCE TO:

<b>MILLEN, WHITE, ZELANO &amp; BRANIGAN, P.C.</b> Arlington Courthouse Plaza 1 2200 Clarendon Boulevard, Suite 1400 Arlington, Virginia 22201 703-243-6333  Filed: 12/20/99 AJZ:jvbp	SIGNATURE _____ <b>Anthony J. Zelano</b> NAME _____ <b>27,969</b> REGISTRATION NUMBER _____ <b>20 December 1999</b> DATE _____
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INTERNATIONAL APPLICATION NO. : PCT/EP98/03250  
 INTERNATIONAL FILING DATE : 30 May 1998  
 PRIORITY DATE CLAIMED : 19 JUNE 1997  
 Applicant(s) (DO/EO/US) : Reiner DELP et al.  
 Title: LASER-MARKABLE PLASTICS

**PRELIMINARY AMENDMENT**

BOX PCT  
 Assistant Commissioner for Patents  
 Washington, D.C. 20231

SIR:

Please amend the above-identified International application as follows prior to calculation of the fees.

**IN THE SPECIFICATION:**

Page 2, line 19: Delete "PE [sic]".  
 Page 5, line 10: Delete "[sic]".  
 Page 6, line 13: Delete "Vol. 15"  
 line 14: Delete "[sic]".  
 Page 8, line 8: Delete "[sic]".  
 Page 9, line 22: Delete "biscuits [sic]" and insert -- platelets --.  
 Page 10, line 16: Delete "biscuits [sic]" and insert -- platelets --.  
 Page 11, line 15: Delete "methyl [sic]" and insert -- polymethyl--.

**IN THE CLAIMS:**

Please amend claims 3-6 and 8-11 as follows:

**Claim 3, lines 1 and 2:** Change "Claim 1 or 2" to -- Claim 1 --.  
**Claim 4, lines 1 and 2:** Change "one of Claims 1 to 3" to -- Claim 1 --.  
**Claim 5, lines 1 and 2:** Change "one of Claims 1 to 4" to -- Claim 1 --.  
**Claim 6, lines 1 and 2:** Change "one of Claims 1 to 5" to -- Claim 1 --.  
**Claim 8, lines 1 and 2:** Change "one of Claims 1 to 7" to -- Claim 1 --.

**Claim 9, lines 1 and 2:** Change "one of Claims 1 to 8" to -- Claim 1 --.

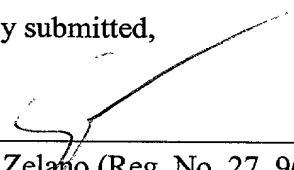
**line 5:** Delete methyl [sic] and replace with polymethyl.

**Claim 10, lines 1 and 2:** Change "one of Claims 1 to 9" to -- Claim 1 --.

### **REMARKS**

The principal purpose of this Preliminary Amendment is to eliminate discrepancies in the text and to eliminate multiple dependencies in order to avoid extra fees.

Respectfully submitted,

  
\_\_\_\_\_  
Anthony J. Zelano (Reg. No. 27, 969)  
Attorney for Applicants

MILLEN, WHITE, ZELANO & BRANIGAN, P.C.  
Arlington Courthouse Plaza I  
2200 Clarendon Boulevard, Suite 1400  
Arlington, Virginia 22201  
Direct Dial: 703-812-5311  
Facsimile: 703-243-6410  
Internet Address: zelano@mwzb.com

**Filed:** 20 December 1999

## Laser-markable plastics

The present invention relates to laser-markable plastics of which a feature is that a plastic which is  
5 difficult to laser-treat comprises as absorber material one or more intrinsically laser-markable polymers in the form of micromilled particles having a particle size of 0.1 - 100  $\mu\text{m}$ .

The labelling of production goods is becoming  
10 increasingly important in almost all sectors of industry. For example, it is frequently necessary to apply production dates, expiry dates, barcodes, company logos, serial numbers, etc. At present, these marks are predominantly made using conventional techniques such  
15 as printing, embossing, stamping and labelling. However, the importance of contactless, high-speed and flexible marking using lasers is increasing, especially in the case of plastics. This technique makes it possible to apply graphic inscriptions, for example  
20 barcodes, at high speed even on a non-planar surface. Since the inscription is within the plastics article itself, it is durable and resistant to abrasion.

Many plastics, for example polyethylene (PE), polypropylene (PP), polyamide (PA), polymethyl meth-  
25 acrylate (PMMA), polyoxymethylene (POM), polyurethane (PUR), polyesters have hitherto proved to be very difficult or even impossible to mark by means of the laser. A  $\text{CO}_2$  laser which emits light in the infrared region at 10.6  $\mu\text{m}$  produces only a faint, barely legible  
30 mark on polyolefins, even at very high output levels, since the absorption coefficient of the plastics to be processed is not high enough at these wavelengths to induce a colour change in the polymeric material. The plastic must not completely reflect or transmit the  
35 laser light, since if it did there would be no interaction. However, there must also not be strong absorption, since in that case the plastic evaporates to leave only an engraving. The absorption of the laser beams and hence the interaction with the material

depends on the chemical structure of the plastic and on the laser wavelength employed. In many cases it is necessary to add appropriate additives, for example absorbers, in order to render plastics laser-inscribable.

The article "Pearl Lustre Pigments - Characteristics and Functional Effects" in Speciality Chemicals, May 1982, Vol.2, No. 2 discloses the use of pearl lustre pigments for laser marking. Pearl lustre pigments, however, have the disadvantage that they severely alter the colour properties of the plastic, an effect which is often unwanted.

DE-A 29 36 926 discloses that the inscription of a polymeric material by means of laser light can be achieved by adding to the plastic a filler, such as carbon black or graphite, which discolours on exposure to energetic radiation.

EP 0 190 997 A prepares laser-inscribable moulding compounds, including PE, PE [sic] or PS, by adding at least one inorganic pigment to the high molecular mass organic material.

In EP 0 330 869,  $\text{TiO}_2$  and carbon black are added to PBT and PET. The inscription is dark on a light background. The use of carbon black and/or graphite as absorbers in connection with the laser marking of polyesters is known from EP 0 485 181.

However, the fillers known for laser marking have the disadvantage either that they permanently colour the plastic that is to be inscribed, and hence the laser inscription, which is usually a dark script on a lighter background, then lacks sufficient contrast, i.e. legibility, or that as in the case, for example, of kaolin the mark is very faint and becomes readily visible only when large amounts of the additive are employed.

DE 195 36 047 describes the use of polycarbonate, which itself is difficult to laser-mark owing to its amorphous structure, in a polymer matrix of a polyalkylene terephthalate. Through absorption of

laser energy it is possible for dark characters to be achieved on a light background in the polymer matrix of a polyalkylene terephthalate.

In addition to the abovementioned plastics, however, there are also polymers which can be marked by means of a laser with darkness and great contrast without the addition of additives. Examples of such polymers include PET, butadiene-styrene (ABS), polystyrene, polyphenyl ether (PPO), liquid crystal polymers (LCP), polyphenylene sulfide, polyarylates, polyaryl sulfides, polyaryl sulfones, polyaryl ether ketones, and blends thereof.

The object of the present invention, therefore, was to find laser-markable plastics which permit high-contrast laser marking on exposure to laser light. In this context, the filler or successful absorber should have a very pale, neutral inherent colour and should possess the properties of the precoloured plastic that is to be marked or should have little or no effect on these properties.

It has surprisingly been found that a plastic which is difficult to laser-treat can be marked very effectively if, for example, one of the abovementioned intrinsically markable polymers is added in fine distribution to the plastic. The intrinsic markability of the polymer is thus transferred to the plastic which shows little if any such behaviour. Following laser bombardment, a plastic doped in this way shows high-contrast and crisply contoured markings even at low laser intensities.

The invention therefore provides laser-markable plastics, characterized in that plastics which are difficult to laser-treat comprise one or more intrinsically markable polymers having a particle size of from 0.1 to 100  $\mu\text{m}$ .

Through the addition of micromilled, intrinsically markable polymers as absorbers in concentrations of 0.1 to 10% by weight, preferably 0.1 to 5% by weight and, in particular, 0.1 to 2% by

weight, based on the plastics system, a high contrast is obtained in connection with laser marking. The concentration of the intrinsically markable polymers in the plastic, however, is dependent on the plastics system employed and on the laser used.

Suitable polymers or polymer mixtures are all known readily laser-treatable plastics, such as PET, ABS, polystyrene, PPO, polyphenylene sulfide, polyphenylene sulfone, polyimidosulfone and LCPs, for example.

Micromilled thermoplastics having a very high melting range of  $>300^{\circ}\text{C}$  are particularly suitable. The crispness of the contours of the mark is determined in particular by the particle size of the micromilled polymers. The polymers preferably have particle sizes in the range from 0.1 to 50  $\mu\text{m}$ , in particular from 1 to 20  $\mu\text{m}$ .

The resulting mark is positively influenced if the intrinsically markable polymer comprises as further absorber, a light-sensitive pigment, such as a filler, for example, a conductive pigment and/or a special-effect pigment. The addition of a further absorber intensifies the contrast as a function of the plastics system used. The amount of light-sensitive pigment added should be between 0.1 and 90%

Particularly suitable light-sensitive pigments are fillers, such as  $\text{TiO}_2$  and  $\text{SiO}_2$ , for example, and phyllosilicates. Suitable silicatic platelets here are, in particular, light-coloured or white micas. It is of course also possible to use other natural micas, such as phlogopite and biotite, synthetic mica, talc flakes and glass flakes. By special-effect pigments are meant all known lustre, metallic and pearl lustre pigments, as marketed, for example, by the companies Mearl, Eckart-Werken and Merck KGaA. Examples of suitable conductive pigments are the pigments marketed under the tradename Minatec® by Merck KGaA. These are platelet-shaped  $\text{TiO}_2$ / mica pigments comprising an external tin/antimony oxide layer as conductive coat. Other



suitable light-sensitive pigments are the oxides, hydroxides, sulfides, sulfates and phosphates of metals such as copper, bismuth, tin, zinc, silver, antimony, manganese, iron, nickel and chromium, for example.

5 Particular mention should be made in this case of the use of antimony, bismuth oxychloride and basic copper(II) hydroxide phosphate. Particular preference in this context is given to a product as formed by heating blue Cu(II) orthophosphate ( $\text{Cu}_3(\text{PO}_4)_2 \cdot 3 \text{H}_2\text{O}$ ) by  
10 heating [sic] to from 100 to 200°C, and which has the empirical chemical formula  $4 \text{CuO} \cdot \text{P}_2\text{O}_5 \cdot \text{H}_2\text{O}$  or  $\text{Cu}_3(\text{PO}_4)_2 \cdot \text{Cu}(\text{OH})_2$ . Other suitable copper phosphates are  
6  $\text{CuO} \cdot \text{P}_2\text{O}_5 \cdot 3 \text{H}_2\text{O}$ ,  $\text{Cu}_3(\text{PO}_4)_2 \cdot 3 \text{Cu}(\text{OH})_2$ , 5  $\text{CuO} \cdot \text{P}_2\text{O}_5 \cdot 3 \text{H}_2\text{O}$ ,  
 $\text{Cu}_3(\text{PO}_4)_2 \cdot 2 \text{Cu}(\text{OH})_2 \cdot \text{H}_2\text{O}$ , 4  $\text{CuO} \cdot \text{P}_2\text{O}_5$ , 4  $\text{CuO} \cdot \text{P}_2\text{O}_5 \cdot 3\text{H}_2\text{O}$ , 4  
15  $\text{CuO} \cdot \text{P}_2\text{O}_5 \cdot 1.5 \text{H}_2\text{O}$ , 4  $\text{CuO} \cdot \text{P}_2\text{O}_5 \cdot 1.2 \text{H}_2\text{O}$ .

An improvement in laser markability is also achieved if, in addition to the intrinsically marking polymer, one or more abovementioned light-sensitive pigments are added as a further component to the  
20 plastic. In this case the proportion by weight of all absorbers in the plastic, in combination with the micromilled polymers, should not exceed a total of 10% by weight, based on the plastics system. The plastic preferably contains 0-5% by weight of light-sensitive  
25 pigments, especially 0-1% by weight. In this context, there is no restriction on the proportion in which the light-sensitive pigments are mixed with the micromilled polymers.

It is also possible to add, to the plastic that  
30 is difficult to laser-treat, colour pigments, which permit colour variations of any type and at the same time ensure that the laser marking is retained.

The light-sensitive pigments and/or colour pigments are added preferably together with the  
35 polymers, although separate addition is also possible in principle. A mixture of different light-sensitive pigments can also be added to the plastic.

Marking is preferably carried out using high-energy radiation, generally in the wavelength range

from 150 nm to 10,600 nm, in particular in the range from 150 nm to 1100 nm. Mention may be made here, for example, of CO<sub>2</sub> lasers (10,600 nm), Nd:YAG lasers (1064 nm or 532 nm) or pulsed UV lasers (excimer lasers). Particular preference is given to the use of Nd:YAG lasers (1064 nm and 532 nm) and CO<sub>2</sub> lasers (10,600 nm). The energy densities of the lasers employed are generally in the range from 0.3 mJ/cm<sup>2</sup> to 50 J/cm<sup>2</sup>, preferably in the range from 0.3 mJ/cm<sup>2</sup> to 10 J/cm<sup>2</sup>.

All known plastics which can only be laser-marked with great difficulty, as are described, for example, in Ullmann, Vol. 15, p. 457 ff., Vol. 15 [sic], Verlag VCH or Saechtling Kunststoff Taschenbuch, can be employed for laser marking through addition of the polymers of the invention. Examples of such plastics are thermosets, polyethylene (PE-HD, PE-LD, PE-LLD), polypropylene (PP), polyesters, polyacetal, polyamides (PA), polyurethanes (PUR), polybutylene terephthalate, polymethyl methacrylate (PMMA), polyvinyl acetal, polystyrene, butadiene-styrene (ABS), acrylonitrile-styrene-acrylate (ASA), and their copolymers and/or mixtures thereof. In particular, polyolefins, polyurethanes, polyoxymethylenes and polyamides, owing to their mechanical properties, the cost-effective processing methods and their poor laser-markability, are suitable for doping with the polymers of the invention.

The incorporation of the micromilled polymer into the plastic takes place by the techniques known for pigments and fillers. Subsequently, the pigmented plastic is then deformed under the action of heat. When choosing the intrinsically markable polymer to be milled it should be borne in mind that the particle structure is retained following the incorporation; in other words, the particles should not be soluble in the melt, and should not melt as well. This is achieved by appropriate tailoring of the melting ranges of the plastics system to that of the micromilled polymer.

When the micromilled polymer is incorporated into the plastics granules it is possible, if desired, to add coupling agents, organic, polymer-compatible solvents, stabilizers, optical brighteners, colour  
5 pigments, dyes, fillers, reinforcing agents, flameproofing additives, antistatics and/or surfactants which are temperature-stable under the operating conditions. In addition to the auxiliaries customarily employed it is possible to add further additives, not  
10 mentioned here, to the plastic. The presence of further additives in the existing plastics systems, however, may exert an effect on the marking result.

The plastics granule/polymer mixture is generally prepared by charging an appropriate mixer  
15 with the plastics granules, wetting them with any additives, and then adding the micromilled polymers and mixing them in. The mixture obtained in this way can then be processed directly in an extruder or an injection moulding machine. The mouldings formed in the  
20 course of processing usually exhibit a very homogeneous distribution of the polymers or of the polymer mixture. Finally, laser marking takes place, preferably with a Nd:YAG laser.

Inscription with the laser is carried out by  
25 introducing the sample into the beam path of a pulsed laser, preferably a Nd:YAG laser. Inscription with a CO<sub>2</sub> laser or an excimer laser is also possible. However, the desired results can also be achieved with other types of laser featuring a wavelength in a range of  
30 high absorption by the intrinsically marking polymer. The resulting shade and depth of colour are determined by the laser parameters, such as the irradiation time and irradiation output. The output of the lasers used depends on the particular application and can be  
35 determined regularly in each individual case by the skilled worker.

The plastic doped in accordance with the invention can be used in all sectors where customary printing processes have hitherto been employed for the

inscription of plastics. For example, mouldings of the plastic of the invention can be employed in the electrical, electronic and motor vehicle industry. The labelling and inscription of, for example, housings, lines, keycaps, transcripts or functional parts in the heating, ventilation and cooling sectors, or switches, plugs, levers and handles which consist of the plastic of the invention, can be marked [sic] with the aid of laser light, even at difficult-to-reach points. Owing to its low heavy-metal content, the plastics system of the invention can also be employed in packaging in the foodstuffs sector or in the toy sector. The markings on packaging are notable for their resistance to wiping and scratching, for their stability during subsequent sterilization processes, and for the fact that they can be applied in a hygienically pure manner in the marking process. Complete label motifs can be applied durably to the packaging for a reusable system. Another important area of application for laser inscription is that of identity cards and plastic tags for the individual identification of animals: so-called cattle tags or earmarks. The laser marking of plastics articles or mouldings which consist of the plastic of the invention is hence possible.

The examples which follow are intended to illustrate the invention without, however, restricting it.

## Examples

### Example 1

- 5    99 parts    of polypropylene (Stamylan PPH 10 from DSM)  
     1 part    of polyphenylene sulfide milled to a particle  
         size < 25  $\mu\text{m}$

     The components are physically mixed and by  
means of an injection moulding machine are homogenized  
10 and shaped to form platelets. The inscription with a  
Nd:YAG laser at 532 and 1064 nm wavelengths shows a  
high-contrast black marking with a smooth surface over  
a wide range of settings.

### 15    Example 2

- 99.5 parts        of polypropylene (Stamylan PPH 10)  
     0.5 part         of polyphenylene sulfone milled to a  
         particle size < 10  $\mu\text{m}$

20       The components are mixed and by means of an  
injection moulding machine are homogenized and shaped  
to form biscuits [sic]. The inscription with a Nd:YAG  
laser shows a high-contrast black marking with a smooth  
surface over a wide range of settings.

25

### Example 3

- 99 parts    of polyamide 6 (Ultramid B3K from BASF)  
     1 part    of polyimidosulfone milled to a particle size  
30           < 15  $\mu\text{m}$

     The components are mixed and by means of an  
injection moulding machine are homogenized and shaped  
to form platelets. The inscription with a Nd:YAG laser  
shows a high-contrast deep-black marking with a smooth  
35 surface over a wide range of settings.

### Example 4

- 99.6 parts        of polyamide 6 (Ultramid B3K)

0.4 part of polyphenylene sulfide milled to a particle size  $< 10 \mu\text{m}$

The components are mixed and by means of an injection moulding machine are homogenized and shaped to form platelets. The inscription with a Nd:YAG laser shows a high-contrast black marking with a smooth surface over a wide range of settings.

Example 5

10

99 parts of polyoxymethylene (Delrin from Du Pont)  
1 part of polyphenylene sulfide milled to a particle size  $< 5 \mu\text{m}$

The components are mixed and by means of an injection moulding machine are homogenized and shaped to form biscuits [sic]. The inscription with a Nd:YAG laser shows a high-contrast black marking with a smooth surface over a wide range of settings.

20 Example 6

99 parts of unsaturated polyester resin (Palatal from BASF)  
1 part of polyphenylene sulfide milled to a particle size  $< 10 \mu\text{m}$

The polyphenylene sulfide is incorporated homogeneously into the liquid polyester casting resin by stirring. Following the addition of accelerator (Co octoate) and hardener (cyclohexanone peroxide), the mixture is poured into a mould. After curing has taken place, a moulding is obtained which can be given a high-contrast black marking by means of Nd:YAG lasers.

Example 7

35 99 parts of polysulfone (Ultrason from BASF) are compounded on an extruder together with 1 part of mica. The compound is micromilled to a particle size of  $< 10 \mu\text{m}$ . 0.5% of the powder thus obtained are added to a PMMA. This mixture is processed on an extruder to

give sheets which can be given a black and high-contrast marking with a Nd:YAG laser at a wavelength of 532 and 1,064 nm.

5 Example 8

96 parts of polyphenylene sulfide are compounded by the method of Example 7 with 4 parts of basic copper phosphate. An addition of just 0.4% of the micromilled powder of this mixture to commonly non-  
10 laser-markable plastics, such as.

- (a) polyethylene (PE)
- (b) polypropylene (PP)
- (c) polyamide (PA)
- 15 (d) methyl [sic] methacrylate (PMMA)
- (e) polyurethane (PU)
- (f) polyoxymethylene (POM)

gives deep-black, high-contrast markings with crisp  
20 contours using a Nd:YAG laser.

### Patent Claims

1. Laser-markable plastics, characterized in that  
5 a plastic which is difficult to laser-mark comprises as  
absorber material an intrinsically laser-markable  
polymer in the form of micromilled particles having a  
particle size of 0.1 - 100  $\mu$ m.
2. Laser-markable plastics according to Claim 1,  
10 characterized in that the absorber material is a high-  
temperature-resistant plastic.
3. Laser-markable plastics according to Claim 1 or  
2, characterized in that the absorber material is  
polyphenylene sulfide, polysulfone, polyarylate,  
15 polyimide, liquid-crystalline polymers or a mixture  
thereof.
4. Laser-markable plastics according to one of  
Claims 1 to 3, characterized in that the proportion of  
the absorber material based on the plastics system is  
20 0.1 - 10% by weight.
5. Laser-markable plastics according to one of  
Claims 1 to 4, characterized in that the particle  
structure of the intrinsically markable polymer is  
retained in the plastic.
- 25 6. Laser-markable plastics according to one of  
Claims 1 to 5, characterized in that the absorber  
material additionally comprises, as further absorber,  
one or more light-sensitive pigments.
7. Laser-markable plastics according to Claim 6,  
30 characterized in that the light-sensitive pigment is  
natural or synthetic mica, copper phosphate, a special-  
effect pigment, a conductive pigment, a metal nitrate,  
metal sulfate, metal sulfide or metal oxide.
8. Laser-markable plastics according to one of  
35 Claims 1 to 7, characterized in that the proportion of  
the light-sensitive pigments in the plastic is from 0  
to 5% by weight, based on the plastics system.
9. Laser-markable plastics according to one of  
Claims 1 to 8, characterized in that the plastic which



is difficult to laser-treat is polyethylene, polypropylene, polyamide, polyoxymethylene, polyester, methyl [sic] methacrylate, polyurethane or a copolymer thereof.

5 10. Laser-markable plastics according to one of Claims 1 to 9, characterized in that they additionally comprise colour pigments.

11. Use of the laser-markable plastics according to Claim 1 as material for producing mouldings which are  
10 marked with the aid of lasers.

12. Mouldings consisting of the laser-markable plastic according to Claim 1.

**Abstract**

The present invention relates to laser-markable  
5 plastics of which a feature is that a plastic which is  
difficult to laser-treat comprises as absorber material  
an intrinsically laser-markable polymer in the form of  
micromilled particles having a particle size of 0.1 -  
100  $\mu\text{m}$ .

Docket No.  
MERCK

# Declaration and Power of Attorney For Patent Application

## English Language Declaration

As a below named inventor, I hereby declare that:

My residence, post office address and citizenship are as stated below next to my name,

I believe I am the original, first and sole inventor (if only one name is listed below) or an original, first and joint inventor (if plural names are listed below) of the subject matter which is claimed and for which a patent is sought on the invention entitled

Laser-markable plastics

the specification of which

(check one)

☐ is attached hereto.

☒ was filed on May 30, 1998 as United States Application No. or PCT International Application Number PCT/EP 98/03250

and was amended on \_\_\_\_\_  
(if applicable)

I hereby state that I have reviewed and understand the contents of the above identified specification, including the claims, as amended by any amendment referred to above.

I acknowledge the duty to disclose to the United States Patent and Trademark Office all information known to me to be material to patentability as defined in Title 37, Code of Federal Regulations, Section 1.56.

I hereby claim foreign priority benefits under Title 35, United States Code, Section 119(a)-(d) or Section 365(b) of any foreign application(s) for patent or inventor's certificate, or Section 365(a) of any PCT International application which designated at least one country other than the United States, listed below and have also identified below, by checking the box, any foreign application for patent or inventor's certificate or PCT International application having a filing date before that of the application on which priority is claimed.

Prior Foreign Application(s)

Priority Not Claimed

<u>DE 197 26 136.1</u>	<u>Germany</u>	<u>19 June 1997</u>	<input type="checkbox"/>
(Number)	(Country)	(Day/Month/Year Filed)	
_____	_____	_____	<input type="checkbox"/>
(Number)	(Country)	(Day/Month/Year Filed)	
_____	_____	_____	<input type="checkbox"/>
(Number)	(Country)	(Day/Month/Year Filed)	

I hereby claim the benefit under 35 U.S.C. Section 119(e) of any United States provisional application(s) listed below:

\_\_\_\_\_  
(Application Serial No.)

\_\_\_\_\_  
(Filing Date)

\_\_\_\_\_  
(Application Serial No.)

\_\_\_\_\_  
(Filing Date)

\_\_\_\_\_  
(Application Serial No.)

\_\_\_\_\_  
(Filing Date)

I hereby claim the benefit under 35 U. S. C. Section 120 of any United States application(s), or Section 365(c) of any PCT International application designating the United States, listed below and, insofar as the subject matter of each of the claims of this application is not disclosed in the prior United States or PCT International application in the manner provided by the first paragraph of 35 U.S.C. Section 112. I acknowledge the duty to disclose to the United States Patent and Trademark Office all information known to me to be material to patentability as defined in Title 37, C. F. R., Section 1.56 which became available between the filing date of the prior application and the national or PCT International filing date of this application:

\_\_\_\_\_  
(Application Serial No.)

\_\_\_\_\_  
(Filing Date)

\_\_\_\_\_  
(Status)  
(patented, pending, abandoned)

\_\_\_\_\_  
(Application Serial No.)

\_\_\_\_\_  
(Filing Date)

\_\_\_\_\_  
(Status)  
(patented, pending, abandoned)

\_\_\_\_\_  
(Application Serial No.)

\_\_\_\_\_  
(Filing Date)

\_\_\_\_\_  
(Status)  
(patented, pending, abandoned)

I hereby declare that all statements made herein of my own knowledge are true and that all statements made on information and belief are believed to be true; and further that these statements were made with the knowledge that willful false statements and the like so made are punishable by fine or imprisonment, or both, under Section 1001 of Title 18 of the United States Code and that such willful false statements may jeopardize the validity of the application or any patent issued thereon.

POWER OF ATTORNEY: As a named inventor, I hereby appoint the following attorney(s) and/or agent(s) to prosecute this application and transact all business in the Patent and Trademark Office connected therewith. (list name and registration number)

3  
 I. William Millen (Reg. No. 19,544)  
 John L. White (Reg. No. 17,746)  
 Anthony J. Zelano (Reg. No. 27,969)  
 Alan E.J. Branigan (Reg. No. 20,565)  
 John R. Moses (Reg. No. 24,983)  
 Harry B. Shubin (Reg. No. 32,004)  
 Brion P. Heaney (Reg. No. 32,542)  
 Richard J. Traverso (Reg. No. 30,595)

Diana Hamlet-King (Reg. No. 33,302)  
 John A. Sopp (Reg. No. 33,103)  
 Richard E. Kurtz (Reg. No. 33,936)  
 Richard M. Lebovitz (Reg. No. 37,067)  
 John H. Thomas (Reg. No. 33,460)

Send Correspondence to: MILLEN, WHITE, ZELANO & BRANIGAN, P.C.  
Arlington Courthouse Plaza I  
2200 Clarendon Blvd., Suite 1400  
Arlington, VA 22201

Direct Telephone Calls to: (name and telephone number)

Full name of sole or first inventor	
Reiner Delp	
Sole or first inventor's signature	Date
<i>[Signature]</i>	September 6, 1999
Residence	
64407 Fränkisch-Crumbach 64293 Darmstadt	
Citizenship	
German	
Post Office Address	
c/o Merck KGaA, 64271 Darmstadt/Germany DEX	

Full name of second inventor, if any	
Jürgen Solms	
Second inventor's signature	Date
<i>[Signature]</i>	September 6, 1999
Residence	
64319 Pfungstadt	
Citizenship	
German	
Post Office Address	
c/o Merck KGaA, 64271 Darmstadt/Germany DEX	

30

Full name of third inventor, if any	
<u>Gerhard Edler</u>	
Third inventor's signature	Date
<i>G. Edler</i>	September 6, 1999
Residence	
<u>65468 Trebur</u>	
Citizenship	
German	
Post Office Address	
<u>c/o Merck KGaA, 64271 Darmstadt/Germany</u> <u>DEX</u>	

Full name of fourth inventor, if any	
Fourth inventor's signature	Date
Residence	
Citizenship	
Post Office Address	

Full name of fifth inventor, if any	
Fifth inventor's signature	Date
Residence	
Citizenship	
Post Office Address	

Full name of sixth inventor, if any	
Sixth inventor's signature	Date
Residence	
Citizenship	
Post Office Address	